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⑤④ **HIGHLY AMORPHOUS OLEFIN TERPOLYMER.**

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DescriptionTechnical Field

5 This invention relates to highly amorphous olefin terpolymers from propylene, 1-hexene, and ethylene in which the ethylene units are incorporated in the polymer chain in a highly random manner. This invention also relates to a process for producing such terpolymers.

Background of the Invention

10 U.S. Patent 4,259,470 teaches a hot-melt, pressure-sensitive adhesive (HMPSA) comprising a propylene/1-butene or 1-pentene/higher alpha-olefin copolymer. The higher 1-olefin is hexene, heptane, octene, nonene, or decene and is present in the copolymers in 5 to 39 mole percent. The copolymer contains 10 to 55 mole percent propylene and 15 to 60 mole percent of either 1-butene or 1-pentene. No mention is made of ethylene in this patent.

15 U.S. Patent 3,954,697 teaches a HMPSA comprising an amorphous propylene/higher 1-olefin copolymer containing 40 to 60 mole percent 1-olefin having a density of 0.85 to 0.86, a glass transition temperature of -30°C to -45°C, and no measurable differential scanning calorimetry (DSC) melting point. Products from the teachings of this patent have a melt viscosity at 190°C of 10.0 to 75.0 Pa·s (10,000 to 75,000 centipoises (cp)).
20 All the products described are copolymers. The only monomers used are propylene and hexene-1 or higher 1-olefins.

None of the above-identified patents teach terpolymers containing ethylene. Prior art references that teach terpolymers containing ethylene do not teach polymers containing hexene (e.g., U.S. Patent 4,415,718). The terpolymers of the present invention are useful as single component hot-melt, pressure-sensitive adhesives
25 useful for tapes, labels, and the assembly of disposable items such as diapers, feminine hygienic napkins, surgical gowns, and surgical drapes.

The terpolymers of the present invention have properties which are particularly advantageous in view of prior art HMPSAs. For example, the terpolymers of this invention have a lower RBSP than the copolymers of the prior art and they can be used on heat-sensitive substrates such as polyethylene films without distorting the film. Therefore a lower application temperature can be used for the terpolymers which greatly expands the areas in which they can be used.
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The terpolymers of this invention are also more economically desirable than certain prior art HMPSAs in that propylene is less expensive than 1-hexene.

Summary of the Invention

35 The present invention is directed to an amorphous terpolymer comprising repeating units from 0.1 to 10 percent by weight ethylene, from 30 to 78 percent by weight propylene, and from 20 or more percent by weight 1-hexene, the terpolymer having a ring and ball softening point of from 75°C to 120°C. The terpolymers are essentially completely amorphous, and lack any crystalline character, in that they have no crystalline melting point as measured by differential scanning calorimetry (DSC).
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The present invention is also directed to a process for producing an amorphous terpolymer comprising continuously polymerizing a mixture of from 0.1 to 10 percent by weight ethylene, from 30 to 78 percent by weight propylene, and from 20 or more percent by weight 1-hexene, in the presence of a catalyst comprising an anionic coordination catalyst and in a solvent medium or liquid monomer without solvent, at a temperature of from 140°C
45 to 250°C and at a pressure of 689 to 34,474 kPa (100 to 5,000 pounds per square inch gauge (psig)).

Detailed Description of the Invention

50 Suitable catalysts include anionic coordination types such as commercially available aluminum-reduced titanium trichloride activated by trituration (AA-TiCl₃), TiCl₄ supported on MgCl₂, and TiCl₃ supported on MgCl₂. Cocatalysts employed are typical aluminum alkyls such as aluminum triethyl (AlEt₃) and aluminum triisobutyl.

Suitable solvents for the polymerization process include aliphatic hydrocarbons such as hexane, heptane, or cyclohexane and aromatic solvents such as toluene or mixed xylenes. A particularly preferred solvent is a petroleum fraction of an aliphatic hydrocarbon mixture having a boiling point range of about 180°C to about
55 220°C commonly referred to as mineral spirits. In some instances, especially where low viscosity amorphous-material is being produced, only the small amount of solvent necessary to introduce the catalyst is required. That is, the solvent is essentially unreacted monomers and molten terpolymer.

Continuous operation is a greatly preferred process, since this yields the highest degree of random incorporation of the three monomers.

Suitable polymerization temperatures are 140°C to 250°C with 150°C to 180°C being the most preferred range. The suitable pressure range is 689 to 34,474 kPa (100 to 5,000 psig). The most preferred range is (750 to 2,000 psig).

The products of the process are essentially completely amorphous. That is, they are greater than 99 percent soluble in boiling hexane and do not have a DSC melting point. Melt viscosities at 190°C range from 0.1 to 100.0 Pa-s (100 to 100,000 cp) when measured by the Thermosel method using a Brookfield Thermosel Viscrometer by procedures substantially as described in American Society for Testing and Materials (ASTM) procedure D-1824-66. Ring and ball softening points (RBSP) range from about 75°C to 120°C. RBSPs can be determined by the procedure substantially as described in ASTM method E-28.

Glass transition temperatures range from about -20°C to about -35°C. Glass transition temperatures can be determined using a differential scanning calorimeter by procedures substantially as described in ASTM Procedure D-3418. Ethylene contents range from 0.1 to 10 percent as determined by material balances across the reactor. Above 10% ethylene, some blocking may be encountered because of higher reactivity of the ethylene. Hexene contents range from 20 percent to 70 percent as determined by infrared spectrum data. Propylene contents range from 30 percent to 78 percent.

Since ethylene is many times more reactive than propylene and 1-hexene, it was completely unexpected that substantial amounts would be incorporated without ethylene blocking occurring. This is apparently one reason why compositions of this invention should be prepared by continuous polymerization techniques. As described previously, the terpolymers prepared according to this invention show no evidence of ethylene blocking even when as much as 10 weight percent ethylene is incorporated in the terpolymer.

The higher degree of random incorporation of ethylene in terpolymers of the present invention has its most dramatic effect on the RBSP. A copolymer made according to the teachings of U.S. Patent 3,954,697 containing 43 mole percent 1-hexene and 57 mole percent propylene has a RBSP of 125°C. A material of similar viscosity made by the present process containing 55 mole percent propylene, 42 mole percent 1-hexene and 3 mole percent ethylene has a RBSP of 115°C. Thus the terpolymers of the present invention are more amorphous and are distinctly different from the product described in the prior art patent.

Also unexpected is the effect of increasing the ethylene content on the 1-hexene requirement to make a product having a given RBSP. 1-hexene is the most expensive of the three monomers. Any method to reduce the 1-hexene requirement results in a lower manufacturing cost. The incorporation of ethylene into the terpolymers of this invention substantially reduces the 1-hexene requirement.

The probe tack of the terpolymers of the present invention is typically between about 400 and about 750 grams. Probe tack can be measured using a Polyken Probe Tack tester at a dwell time of 2 seconds and a carrier speed of 2 centimeters (cm)/second.

Peel strength of the terpolymers of the invention is typically at least about 21.43 Kg/m (1.2 pounds (lb)/inch). Peel strength can be measured according to Pressure Sensitive Tape Council (PSTC) Test-1, "Peel Adhesion for Single Coated Tape, 180° Angle."

Static shear adhesion of the terpolymers of this invention is typically between 0.6 and 25 hours. Static shear adhesion can be measured according to procedures described in PSTC Test-7 "Shear Adhesion (Holding Power)."

Quick stick of the terpolymers of the present invention is typically between about 17.86 to 32.14 Kg/m (1.0 and about 1.8 pound/inch). Quick stick can be measured according to procedures described in PSTC Test-5.

The terpolymers of this invention also typically have no zippering effect and leave no residue. Zippering (also known as "slip-stick") is often noticed when bonded substrates are separated, resulting from areas of poor adhesion alternating with areas of good adhesion.

The terpolymers of the present invention preferably contain from 0.5 to 10.0 percent by weight ethylene, from 30 to 60 percent by weight 1-hexene and from 30 to 65 percent by weight propylene; more preferred is from 1 to 4 percent by weight ethylene, from 48 to 62 percent by weight 1-hexene, and from 35 to 50 percent by weight propylene.

The process for producing the terpolymer is illustrated in the examples. Generally, the process consists of continuously charging the ethylene, propylene, and 1-hexene in ratios to result in the specified quantities into a reactor. Also, catalytic quantities of the catalysts specified above, and solvent specified above are also continuously charged into the reactor. Molten terpolymer may act as solvent to an extent. Temperature in the reactor is maintained at about 140° to about 205°C, preferably at about 150° to about 180°C, and pressure is maintained at about 1379 to 20,684 kPa (200 to about 3,000 psig), preferably at about 5,171 to 13,790 kPa (750 to about 2,000 psig). Average residence times in the reactor is typically about 3.5 hours. Terpolymer as specified herein is continuously withdrawn from the reactor in solution. A typical process is further described in Example 2.

The following examples are submitted for a better understanding of the invention, but should not be interpreted on a limitation thereon. Unless otherwise specified, all parts, percentages, ratios, etc., are by weight.

Example 1 - Comparative

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This example describes the synthesis of propylenehexene-1 copolymer in the continuous process.

A 25.36 liter (6.7-gallon) stirred loop reactor was fed continuously with propylene, hexene-1, mineral spirits, and catalyst in mineral spirits (catalyst mixture or slurry). The copolymer, monomer, and solvent mixture containing catalyst was removed from the reactor continuously to a letdown tank. Unreacted monomers were flash-
10 ed overhead. The copolymer-solvent mixture was filtered to remove solid catalyst particles, alumina bed treated, and finally stripped to remove solvent.

Reactor conditions and monomer conversions were as shown:

Propylene Charge	3.53 x 10 ⁻⁴ kg/s (2.8 Lb/Hr)
Hexene-1 Charge	8.95 x 10 ⁻⁴ kg/s (7.1 Lb/Hr)
15 Mineral Spirits Charge	2.77 x 10 ⁻⁴ kg/s (2.2 Lb/Hr)
Catalyst Charge	6 x 10 ⁻⁷ kg/s (5.0 x 10 ⁻³ Lb/Hr)
Catalyst	LYNX 900 (Catalyst Resources, Inc.)
Cocatalyst	Et ₃ Al
Cocatalyst/Catalyst Mole Ratio	1/1
20 Copolymer Produced	8.44 x 10 ⁻⁴ kg/s (6.7 Lb/Hr)
Propylene Conversion	80.2 Percent
1-Hexene Conversion	61.9 Percent
Reactor Temperature	162°C
Reactor Jacket Temperature	155°C
25 Reactor Pressure	7,171 kPa (1,040 psig)
Stirrer Speed	750 Revolutions Per Minute (RPM)

The propylene-hexene copolymer has a viscosity at 190°C of (17,250 cp) 17.25 Pa·s and a RBSP of 129°C. It contained 45 mole percent (62 weight %) hexene-1 incorporated as determined by both infrared analysis and Carbon 13 nuclear magnetic resonance (NMR). The glass transition temperature was -27.9°C.

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Example 2

The same reactor described in Example 1 was used to prepare this propylene, hexene-1, ethylene terpolymer. Target viscosity at 190°C was (20,000 to 25,000 cp) 20 to 25 Pa·s. Reactor conditions and monomer
35 conversion are shown below:

Propylene Charge	3.62 x 10 ⁻⁴ kg/s (2.87 Lb/Hr)
Hexene-1 Charge	8.93 x 10 ⁻⁴ kg/s (7.09 Lb/Hr)
Ethylene Charge	1.86 x 10 ⁻⁵ kg/s (1.48 x 10 ⁻¹ Lb/Hr)
Mineral Spirits Charge	3.73 x 10 ⁻⁴ kg/s (2.96 Lb/Hr)
40 Catalyst Charge	3.78 x 10 ⁻⁴ kg/s (3.0 x 10 ⁻³ Lb/Hr)
Catalyst	LYNX 900 (Catalyst Resources, Inc.)
Cocatalyst	Et ₃ Al
Cocatalyst/Catalyst Mole Ratio	1/1
Terpolymer Produced	8.19 x 10 ⁻⁴ kg/s (6.5 Lb/Hr)
45 Propylene Conversion	89.9 Percent
Hexene-1 Conversion	61.8 Percent
Ethylene Conversion	96.6 Percent
Reactor Temperature	161°C
Reactor Jacket Temperature	154°C
50 Reactor Pressure	7,171 kPa (1,040 psig)
Stirrer Speed	750 RPM

Terpolymers were obtained at production rates of 8.2 x 10⁻⁴ kg/s (6.51 pounds per hour) in yields of 1,857 kg per kg (1,857 pounds per pound) of Lynx 900 catalyst. The viscosity was 18.5 Pa·s (18,500 cp) at 190°C and the RBSP was 96°C. The product contained 3 percent ethylene based on material balance. It contained
55 49 mole percent (66 weight %) hexene-1 by infrared spectral analysis.

Thus this example shows that incorporation of as little as 3 percent ethylene in the terpolymer lowers the RBSP from 129°C to 96°C. By lowering the 1-hexene content, which is economically desirable, a good balance of PSA properties and physical properties can be achieved as shown in Example 3.

Example 3

Example 1 was shown to serve as a base point to show the effect of using ethylene to reduce the 1-hexene requirement. The sample reactor described in Example 1 was used to prepare this propylene, hexene-1, ethylene terpolymer. Target RBSP was 110°C to 115°C. Target viscosity at 190°C was (20,000 to 25,000 cp) 20 to 25 Pa·s. Reactor conditions and monomer conversion were as shown:

5	Propylene Charge	4.41 x 10 ⁻⁴ kg/s (3.5 Lb/Hr)
	Hexene-1 Charge	7.43 x 10 ⁻⁴ kg/s (5.9 Lb/Hr)
	Mineral Spirits Charge	3.65 x 10 ⁻⁴ kg/s (2.9 Lb/Hr)
10	Ethylene Charge	1.89 x 10 ⁻⁵ kg/s (0.15 Lb/Hr)
	Catalyst Charge	2 x 10 ⁻⁷ kg/s (2.0 x 10 ⁻³ Lb/Hr)
	Catalyst	LYNX 900 (Catalyst Resources, Inc.)
	Cocatalyst	Et ₃ Al
	Cocatalyst/Catalyst Mole Ratio	1/1
15	Terpolymer Produced	7.81 x 10 ⁻⁴ kg/s (6.2 Lb/Hr)
	Propylene Conversion	82.3 Percent
	Hexene-1 Conversion	53.9 Percent
	Ethylene Conversion	92.5 Percent
	Reactor Temperature	164°C
20	Reactor Jacket Temperature	152°C
	Reactor Pressure	7,171 kPa (1,040 psig)
	Stirrer Speed	750 RPM

Terpolymer was obtained at production rates of 7.85 x 10⁻⁴ kg/s (6.23 pounds per hour) in yields of 1117 kg per kg (2,462 pounds per pound) of Lynx 900 catalyst. The viscosity was 23.1 Pa·s (23,100 cp) at 190°C and the RBSP was 112°C. The product contained 2.3 percent ethylene based on material balance. It contained 40.0 mole percent (57 weight %) 1-hexene by infrared spectral analysis. The glass transition temperature was -27°C. The PSA properties are shown in Table I and are comparable to those of Example 1.

Example 4

The copolymer and terpolymer prepared in Examples 1, 2, and 3 were compared and the results are summarized in Table I.

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TABLE I

	<u>Example 1</u>	<u>Example 2</u>	<u>Example 3</u>
<u>Comparison of Propylene-Hexene Copolymers With</u>			
<u>Propylene-Hexene-Ethylene Terpolymers</u>			
Composition			
Weight % Hexene (mole %)	62 (45)	66 (49)	57 (38)
Weight % Ethylene	0	3	2
Viscosity at 190°C, (cp) Pa·s	(17,250) 17.25	(18,500) 18.5	(23,000) 23
RBSP, °C	129	96	114
Probe Tack, grams	608	583	632
180° Peel, (lb/inch) kg/m	(2.4) 42.86	(1.3) 23.22	(2.5) 44.64
Zippering	None	None	None
Residue	None	None	None
Quick Stick, (lb/inch) kg/m	(1.7) 30.36	(1.3) 23.22	(1.1) 19.64
Static Shear Adhesion	17.1	0.6	23.5

Claims

- An amorphous terpolymer comprising repeating units from 0.1 to 10 percent by weight ethylene, from 30 to 78 percent by weight propylene, and 20 or more percent by weight 1-hexene, the terpolymer having a ring and ball softening point of from 75°C to 120°C and no DSC melting point.
- The amorphous terpolymer of Claim 1 having a melt viscosity of from 0.1 to 100.0 pa.s (100 to 100,000 cp) at 190°C.
- The amorphous terpolymer of Claim 1 having a melt viscosity of from 1.0 to 20.0 Pa.s (100 to 20,000 cp) at 190°C, and a softening point of from 80°C to 115°C.
- The amorphous terpolymer of Claim 1 having from 0.5 to 10 percent by weight ethylene, from 30 to 60 percent by weight 1-hexene, and from 30 to 65 percent by weight propylene.
- The amorphous terpolymer of Claim 1 having from 1 to 4 percent by weight ethylene, from 48 to 62 percent by weight 1-hexene, and from 35 to 50 percent by weight propylene.
- A process for producing an amorphous terpolymer comprising continuously polymerizing a mixture of from 0.1 to 10 percent by weight ethylene, from 30 to 78 percent by weight propylene, and 20 or more percent

by weight 1-hexene, in the presence of a catalyst comprising an anionic coordination catalyst and in a solvent medium, at a temperature of from 140°C to 250°C and at a pressure of 689 to 34,474 kPa (100 to 5,000 psig).

- 5 7. The process of Claim 6 wherein said temperature is from 150°C to 180°C and the pressure is from 5,171 to 13,790 kPa (750 to 2,000 psig).

Patentansprüche

- 10 1. Amorphes Terpolymer mit wiederkehrenden Einheiten aus 0,1 bis 10 Gew.-% Ethylen, aus 30 bis 78 Gew.-% Propylen und 20 oder mehr Gew.-% 1-Hexen mit einem Erweichungspunkt, bestimmt nach der Ring- und Kugelmethode von 75°C bis 120°C ohne DSC-Schmelzpunkt.
- 15 2. Amorphes Terpolymer nach Anspruch 1, mit einer Schmelzviskosität von 0,1 bis 100,0 Pa.s (100 bis 100 000 cp) bei 190°C.
3. Amorphes Terpolymer nach Anspruch 1 mit einer Schmelzviskosität von 1,0 bis 20,0 Pa.s (100 bis 20 000 cp) bei 190°C und einem Erweichungspunkt von 80°C bis 115°C.
- 20 4. Amorphes Terpolymer nach Anspruch 1 mit 0,5 bis 10 Gew.-% Ethylen, 30 bis 60 Gew.-% 1-Hexen und 30 bis 65 Gew.-% Propylen.
5. Amorphes Terpolymer nach Anspruch 1 mit 1 bis 4 Gew.-% Ethylen, 48 bis 62 Gew.-% 1-Hexen und 35 bis 50 Gew.-% Propylen.
- 25 6. Verfahren zur Erzeugung eines amorphen Terpolymeren durch kontinuierliche Polymerisation einer Mischung von 0,1 bis 10 Gew.-% Ethylen, 30 bis 78 Gew.-% Propylen und 20 oder mehr Gew.-% 1-Hexen in Gegenwart eines Katalysators mit einem anionischen Koordinationskatalysator sowie in einem Lösungsmittelmedium bei einer Temperatur von 140°C bis 250°C und einem Druck von 689 bis 34 474 kPa.
- 30 7. Verfahren nach Anspruch 6, bei dem die Temperatur bei 150°C bis 180°C und der Druck bei 5 171 bis 13 790 kPa liegt.

35 Revendications

1. Terpolymère amorphe comprenant des motifs formés de 0,1 à 10 % en poids d'éthylène, de 30 à 78 % en poids de propylène, et d'au moins 20 % en poids de 1-hexène, terpolymère ayant un point de ramollissement bille et anneau (RBSP) compris entre 75°C et 120°C et aucun point de fusion mesurable par calorimétrie différentielle à balayage.
- 40 2. Terpolymère amorphe selon la revendication 1 ayant une viscosité à l'état fondu comprise entre 0,1 et 100,0 Pa.s (100 à 100.000 cp) à 190°C.
- 45 3. Terpolymère amorphe selon la revendication 1 ayant une viscosité à l'état fondu comprise entre 1 et 20,0 Pa.s (100 à 20 000 cp) à 190°C et un point de ramollissement compris entre 80°C et 115°C.
4. Terpolymère amorphe selon la revendication 1 ayant de 0,5 à 10 % en poids d'éthylène, de 30 à 60 % en poids de 1-hexène, et de 30 à 65 % en poids de propylène.
- 50 5. Terpolymère amorphe selon la revendication 1 ayant de 1 à 4 % en poids d'éthylène, de 48 à 62 % en poids de 1-hexène, et de 35 à 50 % en poids de propylène.
- 55 6. Procédé pour produire un terpolymère amorphe consistant à polymériser en continu, un mélange comprenant 0,1 à 10 % en poids d'éthylène, de 30 à 78 % en poids de propylène et au moins 20 % en poids de 1-hexène en présence d'un catalyseur comprenant un catalyseur de coordination anionique en milieu solvant, à une température comprise entre 140°C et 250°C et une pression comprise entre 689 et 34 474 kPa (100 à 5000 psig).

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7. Procédé selon la revendication 6 dans lequel la température est comprise entre 150 et 180°C et la pression entre 5171 et 13 790 kPa (750 à 2000 psig).

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